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### **FEATURE ARTICLE**

### Molecular orientation in small-molecule organic light-emitting diodes

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In research on small-molecule organic light-emitting diodes (OLEDs), the molecular orientation in vacuum-deposited amorphous films has been disregarded for around 20 years, and its effects on device performance have not been sufficiently discussed at the microscopic level. Only recently have the intermolecular interaction and subsequent horizontal molecular orientation in OLEDs been investigated and reported. In this article, an overview of the recent studies on molecular orientation in OLEDs is presented. The general properties of molecular orientation of OLED materials are shown, and its significant effects on the electrical and optical properties of devices are discussed to understand device physics and improve the future performance and reliability of OLEDs.

### 1. Introduction

Recently, research on organic electronics has significantly developed, and it is now regarded as a promising field for the future. We can now use some commercial organic light-emitting diode (OLED) displays, and much wider applications are expected.<sup>1</sup> In the near future, it will inevitably be hoped that organic semiconductor devices will be widely used in our daily lives as silicon devices. To reach that point, it is necessary to

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Daisuke Yokoyama obtained his BS and MS in Physical Chemistry from The University of Tokyo in 1998 and 2000, respectively. After working in Fuji Film Corporation as a research staff member for six years, he joined Kyushu University, and conceived and designed the research on molecular orientation in OLEDs. He obtained his PhD degree in Engineering in 2009 and worked as an assistant professor for one year in Kyushu University. He is currently working at Yamagata

University as an assistant professor, and his main research interests are the in-depth analysis of molecular orientation and ordering in organic semiconductor solids and the application of their functionalities to organic optoelectronic devices. achieve high, attractive, and stable performance for these devices.

If we reconsider why silicon devices have such high reliability today, we find that it is because they are based on the sophisticated theory of semiconductor physics for the bulk state of inorganic semiconductor materials.<sup>2</sup> Organic semiconductors, on the other hand, have significantly different properties because they are composed of molecules bound by weak intermolecular interactions. In particular, the films of small-molecule organic semiconductors consist of units of small molecules, and each molecule has specific characteristics as a single molecule, such as geometric and electronic structures, and absorption and emission spectra. Thus, we usually deduce the properties of the solids of organic semiconductor materials from the characteristics of the single molecules before fabricating the thin films or crystals. This means that each molecule in small-molecule organic semiconductors is independent to some degree because electrons are mainly localized within the molecule, though its properties are shifted or changed depending on intermolecular interactions. We have efficiently used this independence to deduce, control, and improve the properties of organic semiconductor films for the development of many new materials.

However, this independence of molecules in small-molecule organic semiconductors also leads to low charge mobility in most of their films. Since the independence means that the interaction between the molecular orbitals of adjacent molecules is not large, the charge transport between them is generally not as efficient as in inorganic semiconductors having a well-defined band structure.<sup>2</sup> In particular, amorphous organic semiconductor films, which are commonly used in small-molecule OLEDs,<sup>3</sup> have much lower charge mobilities than those in other types of organic semiconductors such as single crystals and polycrystals because the molecular orientation and alignment is much more random. Despite this disadvantage in charge transport, small-molecule amorphous organic films are usually used in OLEDs mainly because of many advantages in fabrication of devices with a large area and a high uniformity; that is, the amorphous films have the advantages of (1) nanometre-scale surface smoothness, (2) easy controllability of thickness, (3) no restriction in the choice of underlying layers, and (4) a simple high-purity fabrication process. They make it possible to stack any organic semiconductor layers having different properties orderly in the direction of thickness and achieve higher-order functionalities of organic materials with high stability and durability even under a high electric field.

To improve the charge mobility in small-molecule amorphous organic films with the above advantages, many kinds of amorphous semiconductor materials have been developed. These have contributed very successfully to the continuous improvement of the performance of OLEDs.<sup>4-7</sup> However, when discussing the properties of amorphous organic films and the performance of OLEDs, we have focused mainly on the properties of films and characteristics of single molecules and have not sufficiently considered how molecules are oriented and aligned in the bulk of the films. Since Tang and VanSlyke<sup>3</sup> began research on OLEDs in 1987, it has been taken for granted for around 20 years that molecular orientation in small-molecule OLEDs is generally random and isotropic. To date, this simple assumption of random orientation has been available as a "0th approximation" in OLED research, as shown in Fig. 1. In the early stage of research on OLEDs, it has been more important to simplify the properties of the films as isotropic and find out principal phenomena than to discuss "trivial" details such as the molecular orientation.

Now, however, research on OLEDs has reached maturity. The performance of the devices is now coming close to the theoretical limit,<sup>8</sup> and the technologies for fabrication, evaluation, and analysis have also been developed to a much higher level than in the early stage. At the present stage, we have to investigate and understand the device physics and the underlying chemistry



Fig. 1 "History" of the picture of molecular orientation in OLEDs. Since the beginning of research in OLEDs, the molecular orientation in vacuum-deposited amorphous films has been disregarded for around 20 years (Section 1). The molecular orientation caused by the anisotropy of molecular shapes has been discussed only recently (Section 3). Furthermore, the orientation control by intermolecular interactions was reported more recently, leading to further improvement of the properties of films (Section 5).

beyond the simple assumption to further improve the performance and reliability of OLEDs. Since it is the microscopic view of chemistry that supports the device physics in organic semiconductors, the detailed investigation of molecular states such as molecular orientation and ordering is very important for explaining the relationship between the chemical characteristics of single molecules and the physical properties of the films. This will help build reliable fundamentals of organic devices.

The molecular orientation of OLED materials in vacuumdeposited amorphous films has been reported and discussed only recently. In this article, an overview of the recent studies on molecular orientation in OLEDs will be presented, and the importance of considering the orientation will be demonstrated. First, to understand the structures of molecules in amorphous films, molecular conformation of OLED materials will be covered briefly in Section 2. Then, Section 3 will discuss the general properties of the molecular orientation of OLED materials and the control of the orientation by temperature. In general, molecules in vacuum-deposited amorphous films are horizontally oriented depending on the anisotropy of the molecular shape, and the orientation can be controlled by heating a substrate during deposition. Next, in Section 4, the significant effects of the molecular orientation on both the electrical and optical properties of devices will be demonstrated. The horizontal molecular orientation has positive effects on charge transport and light outcoupling. Furthermore, Section 5 will show the active control of the molecular orientation by intermolecular interactions. Using weak intermolecular hydrogen bonds, it is possible to control the molecular orientation and molecular stacking in vacuum-deposited films to improve the electrical property of OLEDs. Finally, Section 6 will present the summary and future outlook. Through the overview in this article, we can find that an understanding of molecular states such as orientation and ordering is vital to clarifying the mechanism in OLEDs and improving their future performance.

### 2. Molecular conformation of materials

There seem to be two reasons why molecular orientation in amorphous films has been disregarded for a long time in OLED research, even though it is a matter of course in other kinds of organic solids such as polymer films, polycrystalline films, and single crystals. One is the preconceived idea that the molecular orientation in "amorphous" films must be random and isotropic, and the other is the difficulty in finding a proper method to detect the molecular orientation in such films. Because amorphous materials used in OLEDs have many molecular conformation structures, their films do not have a periodic structure with a long-range order that is usually seen in crystalline films. This makes it difficult to investigate the orientation by X-ray diffraction (XRD) measurement or other conventional methods.

On the other hand, the large number of the conformation structures makes the performance of OLEDs highly stable. Since the molecules used in OLEDs usually have multiple conformation structures with a local minimum steric energy, the structures of the molecules in the films are not the same. This avoids crystallization in the films. The films keep an amorphous state with a very smooth surface without roughness or pinholes, which is critical in OLEDs because we have to control holes and electrons in the direction of small thickness under a high electric field.

Therefore, when we discuss the molecular structure in OLEDs, we should always consider that the molecule has multiple structures in the film. Calculation of molecular structures by molecular mechanics<sup>9</sup> is very informative for this. Although the accuracy of the calculation is less than that of a quantum chemical calculation such as a density functional theory (DFT) calculation, it can find all possible conformation structures without a large computational cost. For example, Fig. 2 shows the conformation structures of 4.4'-bis(N-carbazole)-biphenyl (CBP) and 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (a-NPD) obtained by molecular mechanics calculations in free space using an MMFF94s force field.<sup>10-13</sup> Since two aromatic rings connected by a single bond can have two different dihedral angles between them, there are different conformation structures. When the structures symmetrically equivalent to each other are excluded, the CBP molecule has three structures, and the  $\alpha$ -NPD molecule has 12 structures. In general, the number of conformation structures highly depends on the variation of the dihedral angles and the symmetry in the molecule. We have to consider this variation when we discuss in detail the properties of amorphous films based on the characteristics of single molecules.<sup>14</sup> Then, in addition to the variation of the conformation structures, we should also remember that the structures of molecules in amorphous films are slightly different from those in free space, though the analysis of the difference is currently quite difficult.

## 3. Molecular orientation depending on anisotropy of molecular shape

#### 3.1 Variable angle spectroscopic ellipsometry

To analyze the molecular orientation in vacuum-deposited amorphous films, we need a method to detect the anisotropy of this orientation even in a film without a long-range structural order. One of the best methods to detect the molecular orientation in amorphous organic films is variable angle spectroscopic ellipsometry (VASE),<sup>15,16</sup> which can nondestructively determine the optical properties of thin films and the anisotropy in them. Since the specialized details of this method can be read



Fig. 2 Variety of conformation structures of CBP and  $\alpha$ -NPD obtained by molecular mechanics calculation using an MMFF94s force field.

elsewhere,<sup>17</sup> the outline of the principle will be explained briefly here to understand and interpret the experimental results shown later.

Ellipsometry is an analytical method to model the optical properties of thin films through the use of the interference of obliquely incident light, as shown in Fig. 3. A sample film is usually formed on a substrate having a smooth surface. The incident light is linearly polarized, where the plane of the polarization is usually tilted at 45°. This means that the s- and *p*-components of the electric field ( $E_s$  and  $E_p$  in Fig. 3) of the incident light have the same amplitudes and phases. However, because of the multiple interferences in the thin film, the amplitudes and phases of the s- and p-components in the reflected light become different from those in the incident light. Generally, in light having different amplitudes and phases for the s- and p-components, the plane of the polarization rotates as the light propagates (see the red arrows in Fig. 3); the light is elliptically polarized light. The difference in amplitudes between the s- and p-components in the reflected light is monitored as the ellipsometric parameter  $\Psi$ , and the difference in the phases is monitored as the parameter  $\Delta$ . The values of these parameters significantly depend on the optical constants (refractive index nand extinction coefficient k) and thickness of the film and also on the wavelength and incident angle  $\Theta$ . The optical constants generally have different values depending on the wavelength, and many values of  $\Psi$  and  $\Delta$  at multiple wavelengths are usually obtained to make the analysis sufficiently reliable. From the experimental values of  $\Psi$  and  $\Delta$ , it is possible to determine the optical constants and thickness of the thin film. In the analysis, it is also important to keep Kramers-Kronig consistency,<sup>17</sup> which is a required condition that refractive indices and extinction coefficients should necessarily satisfy.

When the optical properties are complicated as in organic semiconductor films, it is preferable to obtain many more values of  $\Psi$  and  $\Delta$  by changing the incident angle and use all the data to get a unique solution in the analysis. This method of obtaining spectra under variable angles is what we call VASE, which makes it possible to analyze the complicated properties of thin films. In particular, the VASE is sensitive to the optical anisotropy in films because light propagating in an anisotropic film feels different optical properties depending on the incident angle. The values of



**Fig. 3** Schematic of variable angle spectroscopic ellipsometry (VASE). By analyzing the properties of the elliptically polarized light reflected by a sample, the optical constants and their anisotropies can be determined. (Reprinted with permission from ref. 32; Copyright 2009, Elsevier.)

 $\Psi$  and  $\Delta$  significantly depend on the anisotropy of the optical constants, and the optical anisotropies in films can be estimated from this dependence. This means that we can determine the anisotropies in the refractive index *n* and the extinction coefficient *k* of the film. The VASE has been applied mainly to polymer films,<sup>18–20</sup> liquid crystals,<sup>21,22</sup> and inorganic films<sup>23,24</sup> to investigate the optical anisotropy in them. Only recently, it has started to be applied to vacuum-deposited amorphous organic films.

For example, when a film has the same optical properties in both two horizontal directions but a different property in the vertical direction, it means that the film has optical anisotropy, where the optical constants (refractive index and extinction coefficient) are different for horizontally and vertically polarized light: ordinary refractive index and extinction coefficient ( $n_o$  and  $k_o$ ) and extraordinary ones ( $n_e$  and  $k_e$ ), respectively, as shown in Fig. 4(a). This anisotropy in the optical constants of organic films is related to the anisotropy of the molecular orientation in them. To make this relationship clear, it is necessary to correlate the optical properties of films with the electronic properties of molecules.

First, the refractive index of a film is directly related to the molecular polarizability and the number density of the molecules in the film via the Lorentz-Lorenz equation,<sup>25</sup> where the higher the molecular polarizability or the number density is, the higher the refractive index is. In amorphous films, the effect of the molecular polarizability is dominant because the densities of the films are not significantly different. The molecular polarizability represents how easily the electrons in the molecule can be moved by an external electric field. It has different values depending on the direction of the external electric field and the direction of motion of the electrons; more precisely, it has a tensor quantity. In the case of linear-shaped organic molecules, for example, the molecular polarizability generally has a larger value in the direction of the long molecular axis than in the other directions (see Fig. 4(a)), because the electrons in an organic molecule can be easily moved within the molecule. Thus, the orientation of molecules with an anisotropic shape can be deduced from the anisotropy in the refractive index of the film.

Next, the extinction coefficient of a film is directly related to the transition dipole moment of the molecule. The extinction coefficient is represented as  $k = (\lambda/4\pi)\alpha$ , where  $\alpha$  is the absorption coefficient of the film and  $\lambda$  is the wavelength of light. Thus, the extinction coefficient represents light absorption and has a larger value in the direction of the transition dipole moment of the molecules. In the case of linear-shaped organic molecules, the transition dipole moment of most of the molecules is along the long molecular axis, though there are exceptions. Thus, we can learn about the orientation of the molecular axis in the film by investigating the anisotropy in the extinction coefficient of the film and the direction of the transition dipole moment of the molecules.

In the analysis of vacuum-deposited amorphous organic films by VASE, the in-plane rotation of the sample usually does not change the result of the analysis even when the film has large anisotropy. This means that the molecular orientation is random in the plane even when the property of the molecular orientation is different between the horizontal and vertical directions, as shown in Fig. 4(b). Since amorphous materials have many conformation structures as discussed in Section 2, the van der Waals intermolecular interactions of amorphous materials is not as strong as that of polycrystalline materials, leading to loose binding of molecules in the amorphous films with no ordered structure in plane. This molecular behavior in amorphous materials is quite different from that in polycrystalline materials, which often shows a vertical orientation caused by strong intermolecular interaction.<sup>26-28</sup>

The orientation of transition dipole moments in amorphous films can be quantified using an orientation order parameter S,<sup>29</sup> which is defined as

$$S = \frac{3\langle \cos^2 \theta \rangle - 1}{2} = \frac{k_{\rm e}^{\rm max} - k_{\rm o}^{\rm max}}{k_{\rm e}^{\rm max} + 2k_{\rm o}^{\rm max}} \tag{1}$$



**Fig. 4** Relationship between the optical anisotropy in films and molecular orientation. (a) Optical anisotropy in vacuum-deposited amorphous organic films and relationship between the optical properties of films and electronic properties of molecules. (b) Schematic of the horizontal orientation of linear-shaped molecules in amorphous films. (c) Orientation order parameter for the films of linear-shaped molecules.

where  $\langle \cdots \rangle$  indicates the ensemble average,  $\theta$  is the angle between the axis of the transition dipole moment and the direction vertical to the substrate surface, and  $k_0^{\max}$  and  $k_e^{\max}$  are the ordinary and extraordinary extinction coefficients at the peak of the band attributed to the transition dipole moment, respectively. When the transition dipole moment is completely along the long molecular axis of a linear-shaped molecules, S = 1 if the molecules are perfectly oriented vertically to the substrate surface, S =0 if they are randomly oriented, and S = -0.5 if they are perfectly oriented horizontally to the substrate surface, as shown in Fig. 4(c). From the values of the ordinary and extraordinary extinction coefficients obtained by the VASE analysis, we can estimate the orientation of the molecular axis quantitatively using eqn (1). It should be mentioned that eqn (1) is derived under the assumption that the band used for this estimation can be attributed only to a single transition dipole moment of the molecule. If it cannot be attributed only to one, as in the case of symmetric planar molecules having two equivalent degenerate transitions, the equation should be modified to include the contributions of the multiple transitions.

#### 3.2 Horizontal molecular orientation in amorphous films

The detection of the optical anisotropy and molecular orientation in a vacuum-deposited amorphous film of OLED materials was first reported by Lin *et al.* in 2004.<sup>30</sup> They applied VASE to the vacuum-deposited films of two blue-emitting ter (9,9-diarylfluorene) materials and reported that the long molecular axis of these molecules was oriented parallel to the substrate surface. Although this report was very important and gave new insight into molecular states in amorphous films and the OLED mechanism, it did not get enough attention from researchers in the field in OLEDs for several years. This is probably because it focused only on the fluorene materials, and also because using



**Fig. 5** Chemical structures of the OLED materials used to investigate the difference in the anisotropy in the molecular orientation.

VASE to study anisotropy was not popular in the field of organic semiconductors at the time.

To show the importance of molecular orientation in OLEDs, it was necessary to study the generality of the molecular orientation in vacuum-deposited films of various kinds of OLED materials. Four years after the first detection, the generality of the molecular orientation was demonstrated by studies of the dependence on molecular structures. In 2008 and 2009, we reported the horizontal molecular orientation in vacuum-deposited amorphous films of various kinds of OLED materials, including emitting, hole transport, and electron transport materials.<sup>31,32</sup> Figure 5 shows some of the materials that we investigated. Some materials have bulky or compact shapes, and others have linear, planar or long-and-winding shapes. The optical anisotropies in their 100-nm films deposited at the rate of 0.2-0.3 nm s<sup>-1</sup> are shown in Fig. 6, where the wavelength dependences of the refractive indices (red) and extinction coefficients (blue) for horizontally (solid) and vertically (broken) polarized light are shown for each material. The values of the orientation order parameter S obtained using eqn (1) are also shown. In this analysis, the ellipsometric parameters  $\Psi$  and  $\Delta$  were measured at seven variable incident angles in the range of 45–75° in steps of 5° to make the analysis highly reliable.

First, in the case of bulky or compact materials such as 1-4, which were developed in the early stage of OLED research, 3,33-35 the optical properties are almost isotropic, and the values of the orientation order parameter are nearly zero. This means that the orientation of the transition dipole moment attributed to the high absorption is almost random in these films. The film of material 1 is almost optically isotropic because of the isotropic molecular shape. Materials 2 and 3 have their large transition dipole moments in the direction from one nitrogen atom to the other, and material 4 has its large transition dipole moment in the direction parallel to the plane of the central triphenylamine group. The results of the VASE analysis show the random orientation of these dipoles in the films. Both the extinction coefficients and the refractive indices are almost isotropic, indicating that the molecular orientation is almost completely random in three dimensions.

Next, the results of materials 5-8<sup>36-39</sup> show the significant dependence of the orientation on molecular length. These molecules all terminate with carbazole groups, and the molecular lengths are different in the order 5 < 6 < 7 < 8. They have large transition dipole moments in the direction of the long molecular axis. We can see the correlation between the molecular length and the optical anisotropy in the films; that is, the longer the molecular length is, the larger the optical anisotropy in the film is. The fact that the ordinary refractive indices and extinction coefficients are higher than the extraordinary ones shows that the molecules are horizontally oriented in the film, as shown in Fig. 4 (b). We also see the clear correlation between the molecular length and the orientation order parameter. These results clearly demonstrate that the linear-shaped molecules are horizontally oriented in the vacuum-deposited amorphous films depending on the molecular length.

Then, from the results of materials **9–12**, which are hole transport materials mainly composed of triphenylamine groups,<sup>40</sup> we see that not only linear-shaped molecules but also the molecules having a planar or long-and-winding shape are



**Fig. 6** Anisotropies in the refractive indices (red) and the extinction coefficients (blue) of the films of the OLED materials in Fig. 5. The solid and broken lines indicate the horizontal and vertical components of the optical constants, respectively. (Reprinted with permission from ref. 31; Copyright 2008, American Institute of Physics and ref. 32; Copyright 2009, Elsevier.)



**Fig. 7** General relationship between the anisotropies of molecular shape and molecular orientation in vacuum-deposited amorphous organic films.

also horizontally oriented in the films. As in materials **5–8**, the orientation order parameter becomes larger as the molecular length gets longer, though these molecules do not have a rigid linear shape because of the variety of the conformation structures, as discussed in Section 2. Although the conformation structures of these materials are quite complicated, the transition dipole moment is along the  $\pi$ -conjugation system of the molecules. Thus, we can still obtain rough information about the molecular orientation.

The results of the VASE analysis of 1–12 clearly demonstrate the generality of the molecular orientation in vacuum-deposited

on Si on Ag on ITO

**Fig. 8** Schematic of horizontal molecular orientation on various kinds of underlying layers and even in an isotropic organic host matrix.

amorphous organic films; that is, the larger the anisotropy of the molecular shape is, the more significant the molecular orientation is, as shown in Fig. 7. This also means that we had overlooked the molecular orientation of various OLED materials even though many materials having a significantly anisotropic molecular shape have been developed in research on OLEDs. It is worthwhile to investigate the molecular orientation of such materials to understand the properties of the films.

It should be noted that the horizontal molecular orientation occurs on any underlying films or substrates.<sup>32</sup> For example, molecules are similarly oriented on a Si substrate, an ITO electrode, a metal layer, and another organic layer as schematically shown in Fig. 8. This characteristic is specific only to vacuumdeposited amorphous films, and cannot be seen in other types of organic layers such as vacuum-deposited polycrystalline films, spin-coated films, or liquid crystals. Thus, we can use the horizontal molecular orientation in amorphous films without any



**Fig. 9** Dependence of the optical anisotropies in the films of **8–10** on deposition rate. The red and blue lines indicate the refractive indices and extinction coefficients for a deposition rate of  $2 \text{ nm s}^{-1}$ , and the black and green lines indicate those for a deposition rate of  $0.02 \text{ nm s}^{-1}$ , respectively. The solid and broken lines indicate the horizontal and vertical components of the optical constants, respectively.

restriction on the underlying layer or the thickness; that is, the orientation can be used effectively in any multilayer OLED structure. Moreover, it is also worth noting that the horizontal orientation of linear-shaped molecules occurs even in an isotropic organic host matrix. This was qualitatively shown by measurement of the edge emissions from 6 wt%-8-doped CBP films with 15 different thicknesses,<sup>32</sup> and a reliable quantitative estimate of the orientation of dopant molecules was done<sup>41</sup> by combining angular dependence measurement of photoluminescence (PL) spectra and optical simulation.42-44 Since emitting molecules in OLEDs are usually doped in host materials to avoid a concentration quenching, the horizontal orientation in a doped matrix is important when we want to use the orientation of emitting molecules to improve OLED performance. Its effect on optical performance of OLEDs will be discussed in Section 4.2.

Furthermore, we need to know the dependence of the horizontal orientation on the deposition rate to make fabrication processes highly reliable under different conditions. The dependence is shown in Fig. 9, where the optical constants at the higher deposition rate (2 nm s<sup>-1</sup>) and the lower one (0.02 nm s<sup>-1</sup>) are shown for materials **8–10**. The anisotropies of the orientation become slightly smaller with decrease of the deposition rate, but the anisotropies do not change very much even when the deposition rate changes by two orders. This means that we can reproduce the films with similar orientations even if the deposition rate fluctuates to some degree.

Although the dependence on thickness is also important, it is not significant. Since amorphous films do not have a long-range structural order, the effect of the underlying layer does not reach far into the bulk of the films. This is one reason why the orientation can occur on any underlying layer. This homogeneity of orientation in the direction of thickness was demonstrated by *in situ* ellipsometry,<sup>45</sup> shown in the next section. However, there remains a possibility that the molecules show different behavior in their orientation just near an underlying layer. Since the orientation just at the interface cannot be investigated by VASE, the difference in the molecular orientation such as in an initial monolayer on the surface should be discussed carefully by other methods.

From the above results and discussions, it is reasonable to assume that the molecular orientation in amorphous films is caused simply by weak van der Waals interactions between a substrate and molecules and between adjacent molecules.



Fig. 10 Schematics of the orientation mechanism. (a) Vertical orientation of vacuum-deposited polycrystalline materials due to crystallization. (b) Horizontal molecular orientation of vacuum-deposited amorphous materials. (c) Randomization of molecular orientation by deposition on a heated substrate.

Typical mechanisms of the molecular orientations in vacuumdeposited polycrystalline and amorphous films are schematically shown in Fig. 10(a) and (b), respectively.<sup>32</sup> For example, in the case of a polycrystalline film of  $\alpha$ -sexithiophene  $(\alpha$ -6T)<sup>26</sup> on silicon dioxide, molecules are horizontally oriented just after the deposition of a monolayer to reduce the surface energy of the substrate. However, the molecules stand up vertically during the subsequent deposition due to the strong interaction between adjacent molecules and form polycrystalline islands while keeping the high coverage of the substrate surface.<sup>46</sup> This is why molecules in vacuum-deposited polycrystalline films are often vertically oriented.26-28 In amorphous films, on the other hand, since the molecules have a variety of conformation structures, the van der Waals intermolecular interaction is not as strong as that of polycrystalline materials. Thus, the horizontal molecular orientation is kept as a metastable glassy state in the films. This simple mechanism is highly possible because it is consistent with the above experimental results: the simple relationship between the orientation and molecular shapes, the orientation on any underlying layer and in doped films, and the homogeneity of orientation in the direction of thickness.

#### 3.3 Orientation control by deposition on heated substrate

To control the physical properties of vacuum-deposited amorphous organic films, the molecular orientation should be controlled by an experimental condition during fabrication. One method to control it is deposition on heated substrates.<sup>45,47</sup> It is well-known that the morphology and properties of vacuumdeposited amorphous films change and often degenerate when the temperature of the films goes over the glass transition temperature  $T_{g}$ .<sup>48,49</sup> This also means that it is difficult to change the physical properties of the films under  $T_g$  after the deposition without a change in the morphology of the film. Although it was reported that molecular orientation of fluorene materials in amorphous films can be controlled by heating a substrate to over  $T_{g}$  in an inert atmosphere after deposition,<sup>50</sup> heating to over  $T_{g}$  in general inevitably involves changes in the morphology, such as crystallization, increase of surface roughness, or generation of pinholes. Thus, it is preferable to control the properties of amorphous films under  $T_{\rm g}$ .

By heating a substrate during deposition, we found that the molecular orientation in amorphous films can be controlled even under  $T_g$  without crystallization, because molecules on the surface during deposition can locally migrate more readily than in the bulk after deposition.<sup>47,51</sup> Figure 11 shows the optical anisotropies in the 100-nm films of materials **8–10** deposited on

a Si substrate at different temperatures. Although the molecules are horizontally oriented when they are deposited at room temperature, the orientation becomes more random with increase of the substrate temperature under  $T_{g}$  during deposition, as schematically shown in Fig. 10(c). This result means that "the  $T_{g}$  at the surface" of an organic film is lower than that in the bulk. Moreover, in the case of 8, which has a lower  $T_g$  (116 °C) than those of 9 and 10, the direction of the molecular orientation changes to vertical at a substrate temperature of 110 °C without crystallization in the film. This result shows that we can control the molecular orientation in vacuum-deposited amorphous films from horizontal to vertical even at temperatures lower than  $T_{g}$ . In addition, the controllability of the orientation by substrate temperature depends on the roughness of the substrate surface.<sup>47</sup> The control by substrate temperature becomes inefficient when increasing the roughness because the roughness prevents the molecules on the surface from migrating locally.

A more detailed analysis of the control during deposition can be performed by *in situ* ellipsometry. This technique has been applied mainly to inorganic layers,<sup>52,53</sup> and it had not been applied to organic layers during vacuum deposition until recently.<sup>45,54,55</sup> An example of a measurement system is shown in Fig. 12(a) and (b), where an ellipsometer with high response speed is attached to a deposition chamber.<sup>45</sup> The ellipsometric parameters  $\Psi$  and  $\Delta$  can be measured every several seconds during deposition. Using this system, it is possible to track the orientation during deposition; for example, we can investigate the dependence of the orientation on the film thickness. Although the ellipsometric parameters are measured at a single incident angle, measuring them many times every several seconds during deposition increases the reliability of the results.



Fig. 11 Dependence of the optical anisotropies in the films of 8–10 on substrate temperature during deposition. The red and blue lines indicate the refractive indices and extinction coefficients, and the solid and broken lines indicate the horizontal and vertical components of the optical constants, respectively. (Reprinted with permission from ref. 45; Copyright 2010, American Institute of Physics.)



**Fig. 12** In situ ellipsometry measurement during deposition. (a) Structure of the *in situ* ellipsometry system to measure ellipsometric parameters during deposition. (b) Photograph of an example of the system. (c) Schematic of the multilayer structure using a single material. (Reprinted with permission from ref. 45; Copyright 2010, American Institute of Physics.)

Furthermore, this system is useful for analyzing the change of the orientation in detail. An interesting example is shown in Fig. 12(c), where the randomly oriented film of a linear-shaped molecule was deposited at a high substrate temperature, and the horizontally oriented film was subsequently deposited on it at room temperature using the same material after cooling it.<sup>45</sup> By *in situ* ellipsometry, we can nondestructively analyze such a "multilayer" structure using a single amorphous material by modeling separated layers of the same material with different optical properties.

# 4. Effects of molecular orientation on device performance

#### 4.1 Electrical properties

The horizontal molecular orientation causes positive changes in both the electrical and optical properties of OLEDs. First, we focus on the effects of the horizontal molecular orientation of charge transport materials on the electrical properties of OLEDs.

The electrical properties of amorphous films have been widely studied to enhance the performance of OLEDs, and the fundamental mechanisms of carrier injection and transport have been discussed using simple physical models that have also been used in inorganic semiconductor physics.<sup>2,56</sup> Furthermore, in the study on organic semiconductor devices, the Marcus theory<sup>57–59</sup> and Bässler's formalism<sup>60–62</sup> have often been used to discuss the electrical properties of the films; the former is used to discuss the charge transfer between two adjacent molecules in the microscopic view of chemistry, and the latter is used to discuss the randomness of the energy levels and intermolecular distances in the macroscopic view of physics. However, when these theories have been used to discuss the properties of vacuum-deposited amorphous organic films, the molecular orientation or ordering in the films has not been sufficiently considered. Molecular orientation in organic semiconductor films inevitably affects the charge transport characteristics in the films, such as via charge-transfer integrals including intermolecular  $\pi$ - $\pi$ overlap in the Marcus theory<sup>57</sup> and/or energetic and positional disorders in Bässler's formalism.<sup>60</sup> Actually, the effects of molecular orientation and alignment on electrical properties are often discussed for other types of organic solids, such as single crystals,<sup>63-65</sup> polymer films,<sup>66,67</sup> and liquid crystals.<sup>68,69</sup> However, the effects of the molecular orientation in amorphous films have generally not been considered for a long time because the molecular orientation itself has been ignored.

Now, the molecular orientation in vacuum-deposited amorphous organic films is generalized as shown in Section 3.2. Thus, it is natural to think that the molecular orientation affects the electrical properties even of amorphous films. Since the horizontal molecular orientation of charge transport materials causes an increase of  $\pi$ - $\pi$  overlap between adjacent molecules and a decrease of the positional disorder in the film,<sup>70</sup> it improves the charge transport characteristics of the films. There are roughly two ways to demonstrate this effect in amorphous films.

One way is to compare the electrical properties of the films of two similar materials where only the molecular orientations of the molecules are different. To explain the correlation between the molecular orientation and the electrical properties, it is



**Fig. 13** Effect of the molecular orientation of oxadiazole electron transport materials on electron mobility. (a) Anisotropies in the refractive indices (red) and the extinction coefficients (blue) of the films of OXD7 and Bpy-OXD. The solid and broken lines indicate the horizontal and vertical components of the optical constants, respectively. (b) Schematics of the enhancement of electron transport by horizontal orientation of Bpy-OXD molecules. (Reprinted with permission from ref. 71; Copyright 2009, American Institute of Physics.)

important to select two materials having similar single-molecule characteristics and focus on the difference in the molecular orientation independently of the characteristics of the single molecules. A typical example is shown in Fig. 13.<sup>71</sup> The two materials are electron transport materials of oxadiazole derivatives, 1,3-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene (OXD7)<sup>72</sup> and 1,3-bis[2-(2,2'-bipyridin-6-yl)-1,3,4-oxadiazo-5-yl] benzene (Bpy-OXD).<sup>73,74</sup> The central part of an oxadiazole group is common to both molecules. The conformation structures, the distribution of the lowest unoccupied molecular orbitals (LUMOs), and their reorganization energies are also quite similar. This means that the difference in the electronic structures of the LUMOs is quite small between the two derivatives.

However, the electron mobility in the vacuum-deposited films of Bpy-OXD is 30 times higher than that of OXD7.<sup>71</sup> This difference in the electron mobilities cannot be explained by the difference in the electronic structures of the LUMOs of the single molecules. It was shown by ellipsometry that the reason is not the difference in the characteristics of the individual molecules but the difference in the molecular orientations in the films. The orientations of these molecules in vacuum-deposited films are quite different because the terminal groups of the molecules are different. Since the OXD7 molecule has the bulky tert-butyl terminals, the OXD7 film is almost optically isotropic as shown in Fig. 13(a), meaning that the molecular orientation is random in the film. On the other hand, since the 2,2'-bipyridyl terminals of Bpy-OXD are completely planar due to the intramolecular C-H…N interaction, the Bpy-OXD molecule has planar conformation structures. This leads to significantly large anisotropy of molecular orientation in the film. The large difference between ordinary and extraordinary optical constants means that the molecular planes of Bpy-OXD molecules are significantly oriented parallel to the substrate surface. The planar bipyridyl terminals of Bpy-OXD do not significantly affect the electronic structure of the LUMO but contribute largely to the horizontal molecular orientation in the film. This horizontal orientation of the Bpy-OXD molecular plane significantly enhances electron



**Fig. 14** Effect of molecular orientation of the linear-shaped BSB-Cz molecules (material **8**) on hole and electron mobilities. The orientation was controlled by the substrate temperature during deposition. (Reprinted with permission from ref. 47; Copyright 2010, Wiley-VCH.)

transport as a consequence of the large intermolecular overlap of the LUMOs, as shown in Fig. 13(b).

The other way to demonstrate the effect of molecular orientation on electrical properties is to compare the electrical properties of films of the same material where the orientation was controlled during deposition by heating the substrate. This is a more direct investigation of the effects of molecular orientation because the same material is used for the comparison. An example is shown in Fig. 14,47 where the molecular orientations of the linear-shaped BSB-Cz molecules (material 8 in Fig. 5) were controlled during deposition by heating the ITO substrate, as shown in Section 3.3. In this case, because the ITO surface was rougher than the surface of the Si substrate, the change of orientation on the ITO substrate by heating is smaller than that on the Si substrate at the same temperature (see Fig. 11). Thus, the orientation on the ITO substrate becomes random by heating the substrate at 110 °C during deposition, whereas the molecules are horizontally oriented at a substrate temperature of 25 °C. Figure 14 shows the difference in hole and electron mobilities between the horizontally oriented and randomly oriented films. Both the hole and electron mobilities in the horizontally oriented film are higher than those in the randomly oriented film, demonstrating the significant effect of molecular orientation on the electrical properties of vacuum-deposited amorphous organic films.

Since the horizontal molecular orientation occurs even in a multilayer OLED structure as discussed in Section 3.2, the orientation generally affects the electrical properties of OLEDs. To further understand and improve the electrical properties of OLEDs, we should always consider that the molecules of charge transport materials are horizontally oriented in general, and that the orientation affects the electrical properties of the films.

#### 4.2 Optical properties

The horizontal orientation of emitting molecules positively affects the optical properties of OLEDs because the horizontal orientation of the transition dipole moments enhances the light outcoupling efficiency of OLEDs. Since molecules emit light mainly in the direction perpendicular to its transition dipole moment, the horizontal molecular orientation is preferable to the vertical orientation for high light outcoupling efficiency of OLEDs. This is schematically shown in Fig. 15(a), where the emitted light from vertically oriented molecules is almost confined inside the device due to the total reflection at the transparent electrode/glass or glass/air interface. The horizontal molecular orientation leads to a decrease of the number of vertically oriented molecules that cannot contribute to the light outcoupling, resulting in the enhancement of light outcoupling efficiency of OLEDs without a significant change of the angular distribution of the emission. This effect has already been discussed in studies of polymer OLEDs,75 where the molecular orientation of emitting polymers is a matter of course. It was estimated that the light outcoupling efficiency of polymer OLEDs with horizontally oriented emitters can be more than 1.5 times higher than that with randomly oriented emitters.75,76

Since the emitting molecules can be horizontally oriented even in vacuum-deposited amorphous films, it is possible to enhance the light outcoupling efficiency of small-molecule OLEDs using



Fig. 15 Effect of the horizontal orientation of emitting molecules. (a) Schematic of the enhancement of outcoupling efficiency of OLEDs by horizontal orientation of the transition dipole moment of emitting molecules. Since the light is emitted mainly in the direction vertical to the transition dipole moment, the horizontal orientation is preferable for high outcoupling efficiency. (b) Chemical structures of BDAVBi and PEBA used for the comparison of horizontally and randomly oriented emitters. The arrows roughly indicate the direction of the transition dipole moment.

emitting materials having an anisotropic molecular shape causing horizontal orientation. As was mentioned in Section 3.2, the fact that the horizontal orientation can occur even in a doped film is very important because the emitting molecules in OLEDs are usually doped in the host materials to avoid concentration quenching.

The effect of the horizontal orientation on the light outcoupling of small-molecule OLEDs was shown experimentally by comparing two blue-emitting OLEDs with horizontally and randomly oriented emitters.<sup>77</sup> In this comparison, the horizontally oriented emitter was a linear-shaped molecule of 4,4'-bis[4-(diphenylamino)styryl]biphenyl (BDAVBi),<sup>78</sup> whose transition dipole moment is highly oriented to the horizontal direction in doped emitting layer having CBP host matrix in OLEDs,<sup>41</sup> and the randomly oriented emitter was a rather compact molecule of 4-(2,2-diphenylethenyl)-N,N-bis(4-methylphenyl)benzenamine (PEBA),<sup>79</sup> as shown in Fig. 15(b). The PL quantum efficiencies and PL spectra of their doped films were not very different, and the electrical properties of the OLEDs using the doped films as the emitting layer were also quite similar, but the external quantum efficiencies (EQEs) of the OLEDs were significantly different because of the difference in the molecular orientation of the emitting molecules. The light outcoupling efficiency of the OLEDs with the BDAVBi emitter was estimated to be 1.45 times higher than those of the OLEDs with PEBA emitters, indicating the significant effect of the horizontal orientation of the emitting molecules on the light outcoupling efficiency of OLEDs.

This effect on the light outcoupling efficiency is critical to discussing the upper limit of the performance of OLEDs. It also provides us with valuable guideline for developing a new emitting material for high OLED performance. Using the horizontal orientation of emitting molecules, we can expect a light outcoupling efficiency of more than 30%, which is much higher than the value of around 20% that has been thought to be typical.<sup>44,80,81</sup> Since the EOE of OLEDs is currently reaching the theoretical limit, while the maximum internal quantum efficiency is almost unity,<sup>82,83</sup> the enhancement of the light outcoupling efficiency without any complicated outcoupling structure<sup>80,81,84-88</sup> is especially important to improve the performance while keeping the fabrication process simple. In addition, to achieve extremely high EQEs of OLEDs, horizontal orientations of both fluorescent and phosphorescent emitters are very desirable. Most recently, horizontally oriented phosphorescent emitters were discussed and carefully demonstrated<sup>89</sup> by the combining angular dependence measurement of PL and electroluminescence spectra and optical simulation.90,91

# 5. Further active control by intermolecular interactions

Intermolecular interaction between organic molecules<sup>92</sup> is one of the most vital characteristics of organic materials when compared with inorganic materials. In particular, the variety of hydrogen bonds<sup>93,94</sup> plays an essential role in controlling higherorder structures in both chemistry and biology and has also contributed to maximizing the functionalities of organic materials, which cannot be achieved using inorganic materials.<sup>95</sup> Thus, using intermolecular interactions more actively to control molecular orientation and ordering<sup>96–98</sup> seems to be a promising next step in improving device performance (see Fig. 1).

Recently, we showed that intermolecular C–H···N hydrogen bonds can be formed even in vacuum-deposited films having a flat interface, and that the molecular stacking induced by these bonds improves carrier mobility.<sup>14</sup> In Fig. 16(a), four electron transport materials named B0, B2–B4PyMPM are shown, which were used to investigate the effects of intermolecular hydrogen bonds in vacuum-deposited organic films. Some of them were used as electron transport materials in extremely high-performance OLEDs.<sup>99</sup>

The analysis by VASE was performed to study the optical anisotropies in the vacuum-deposited films of these materials, and only the films of B3 and B4PyMPM were found to have singularly large optical anisotropies as shown in Fig. 16(a). Although the molecular shapes of these four materials are quite similar, a singular difference in optical anisotropies was observed depending on the position of the nitrogen atoms in the pyridine rings. The much larger ordinary (horizontal) components of the refractive indices and extinction coefficients of the B3 and B4PyMPM films mean that the molecular planes of these molecules are nearly parallel to the substrate surface. Then, the absorptions of the vertically incident light by the B3 and B4PyMPM films were higher than those by the B0 and B2PyMPM films, though absorptions by solutions with the same concentrations were almost the same for all four materials, as shown in Fig. 16(b). This shows that the transition dipole moments of the B3 and B4PyMPM molecules are horizontally



**Fig. 16** Singularly large anisotropies in B3 and B4PyMPM films by molecular stacking. (a) Refractive indices (red) and extinction coefficients (blue) of B0PyMPM and B2–B4PyMPM films. The solid and broken lines indicate the horizontal and vertical components of the optical constants, respectively. (b) Absorption spectra of 100-nm deposited thin films and solutions with a concentration of  $10^{-5}$  M of B0PyMPM and B2–B4PyMPM. (c) Out-of-plane XRD patterns of B0PyMPM, B2–B4PyMPM, and  $\alpha$ -6T films. The patterns of B3 and B4PyMPM have a halo band, whose peak angle shows the distribution center of the distance of the molecular stacking (red arrow). (Reprinted with permission from ref. 14; Copyright 2011, Wiley-VCH.)

oriented in the films. Furthermore, the out-of-plane XRD patterns of the films suggest the formation of short-range order in the direction of thickness in the B3 and B4PyMPM films. Figure 16(c) shows the out-of-plane XRD patterns of the B0PyMPM, B2–B4PyMPM, and  $\alpha$ -6T films, where the  $\alpha$ -6T film was used as a reference to show the pattern of a polycrystalline film having long-range order.<sup>26</sup> The patterns of the B3 and B4PyMPM films have a broad halo peak around  $2\theta = 23^{\circ}$ , which shows a periodic structure (~3.8 Å) with short-range order formed in the direction of thickness. This shows that the singular horizontal orientation of the B3 and B4PyMPM molecules causes the molecular stacking in the films.

The origin of the singular orientation in the B3 and B4PyMPM films is the intermolecular C-H···N hydrogen bonds between pyridine rings of adjacent molecules.<sup>14</sup> Infrared (IR) absorption spectra of the B2-B4PyMPM films, shown in Fig. 17(a), are informative for investigating and discussing this origin. Because the nitrogen atoms in the pyridine rings in B3 and B4PyMPM are at the outer side of the molecule, they can be connected by intermolecular C–H $\cdots$ N hydrogen bonds as shown in Fig. 17(b), causing a blue-shift of the IR absorption frequency of the C-H stretching modes<sup>100–103</sup> at the neighbor of the nitrogen atoms in the spectra. These spectral shifts show that the intermolecular C-H…N hydrogen bonds in the B3 and B4PyMPM films induce molecular orientation and stacking. Similar intermolecular C-H...N hydrogen bonds and subsequent two-dimensional networks were also directly observed by scanning tunnelling microscope measurement using similar molecules,<sup>104-108</sup> though the networks were a monolayer at the interface between a solution and a graphite surface.

The molecular stacking induced by the intermolecular hydrogen bonds enhances the electron transport in the films.



Fig. 17 Intermolecular C–H···N hydrogen bonds in films. (a) Spectral blue-shift of IR absorption by the formation of intermolecular C–H···N hydrogen bonds in the B3 and B4PyMPM films. (b) Examples of possible interactions between B3PyMPM molecules and between B4PyMPM molecules by intermolecular C–H···N hydrogen bonds. (Reprinted with permission from ref. 14; Copyright 2011, Wiley-VCH.)

Figure 18(a) shows that the electron mobilities of these materials significantly depend on the positions of the nitrogen atoms in the pyridine rings. The electron mobilities at an electric field of  $6.4 \times 10^5 \text{ V cm}^{-1}$  are  $1.6 \times 10^{-6}$ ,  $1.5 \times 10^{-5}$ , and  $1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for B2, B3, and B4PyMPM films, respectively, and the energetic disorders  $\sigma$  and the positional disorders  $\Sigma$  in these films are in the order  $\sigma_{B2} \approx \sigma_{B3} > \sigma_{B4}$  and  $\Sigma_{B2} > \Sigma_{B3} \approx \Sigma_{B4}$ .<sup>109</sup>

Generally, the energetic disorder in a film increases with an increase in the local field caused by the permanent dipole



**Fig. 18** Effects of molecular orientation by intermolecular hydrogen bonds on electron mobility. (a) Dependences of electron mobilities of B2– B4PyMPM films on electric field obtained by time-of-flight measurements at 298 K. (b) Schematic of the effects of molecular orientation and the permanent dipole moment on the electrical properties of the B2– B4PyMPM devices. The B3 and B4PyMPM molecules are bound by the intermolecular hydrogen bonds and form the stacking structure in the films. The arrows in the molecules indicate the large permanent dipole moments of B2 and B3PyMPM. (Reprinted with permission from ref. 14; Copyright 2011, Wiley-VCH.)

moments of the molecules, and the positional disorder increases as the packing constraints between the molecules weaken.<sup>70</sup> Thus, because the B4PyMPM molecules have smaller permanent dipole moments than those of the B2 and B3PvMPM molecules,<sup>14</sup> the energetic disorder in the B4PyMPM film is less than those in the B2 and B3PyMPM films. Then, because the B3 and B4PyMPM molecules are horizontally oriented in the films, the positional disorders in these films are less than that in the B2PyMPM film. These differences in the disorders lead to the significant difference in the electron mobilities  $\mu$  in the B2– B4PyMPM films with the order  $\mu_{B2} < \mu_{B3} < \mu_{B4}$ , as schematically shown in Fig. 18(b). This result shows the significant effects of both the molecular orientation and the permanent dipole moment on the electrical characteristics of OLEDs. It also shows that we can control the molecular stacking via the intermolecular hydrogen bonds even in vacuum-deposited organic films to improve the performance of OLEDs. Furthermore, this result provides us with a new strategy and much insight for developing new materials for construction of an internal self-assembly structure in vacuum-deposited organic films.

#### 6. Summary and outlook

In this article, the studies on horizontal molecular orientation in OLEDs have been briefly reviewed. Starting with the first detection of the molecular orientation of fluorene derivatives, the molecular orientation of various kinds of OLED materials have been investigated systematically. We have demonstrated the general relationship between the anisotropy of molecular structures and the horizontal molecular orientation; the larger the structural anisotropy is, the more significant the horizontal molecular orientation becomes. For applications to OLEDs, it is also noteworthy that the orientation occurs on any underlying layer and even in doped films and is almost homogeneous in the direction of thickness. By heating the substrate during

deposition, the molecular orientation can be controlled even under the glass transition temperature of the material. We have also demonstrated that the horizontal orientation can improve both the electrical and optical properties of OLEDs. The horizontal molecular orientation of charge transport materials enhances the charge transport in the films, and the horizontal molecular orientation of emitting molecules enhances the light outcoupling efficiency of OLEDs. Furthermore, we have shown that the molecular orientation can be controlled more actively using intermolecular C–H…N hydrogen bonds to improve the electrical properties of films. These results will be helpful in understanding device physics and developing new materials for further improving the performance of OLEDs and other organic devices.

Although the various properties of the molecular orientation in OLEDs have been found and studied, there remain many challenging issues for the future. To construct reliable fundamentals of organic devices, it is very important to clarify the detailed structure and ordering of the molecules in the films and their effect on the electrical and optical properties of devices. The followings are the target issues to be solved next.

#### (1) Orientation of functional groups in molecules

As shown in this article, the molecular orientation in OLEDs has been investigated by VASE using UV and visible light, but we can only know the anisotropies of the molecular axis roughly. Although the anisotropies of the molecular polarizability and transition dipole moment can be discussed from the results of VASE in the UV and visible region as shown in Section 3.1, the orientation of each functional group in the molecules has not been the focus of sufficient discussion. When discussing the effect of the orientation of emitting molecules on the light outcoupling of OLEDs, we only have to know the orientation of the transition dipole moment of the emitting molecules. However, when we want to elucidate the effect of the molecular orientation on the electrical properties of the film at the microscopic level, we need to study deeply the orientation not only of the molecular axis but also of functional groups in the molecules. Such an investigation also leads to the elucidation of the difference in the molecular structures in free space and vacuum-deposited amorphous films. One of the methods to solve this issue is analyzing the orientation of the vibrational modes of functional groups using IR light.<sup>110-112</sup> Since IR spectra are not sensitive to the difference in conformation structures,<sup>14</sup> we can discuss the orientation of functional groups without bothering about the variety of the conformation structures. Now, we are investigating the orientation of functional groups of OLED materials using IR-VASE,<sup>16,113-115</sup> where an IR light source and an interferometer are attached to a VASE system.

#### (2) Effect on charge injection at interfaces

It is reasonable to believe that the horizontal molecular orientation affects not only the charge transport in the bulk of films but also the charge injection at an electrode/organic or organic/ organic interface as schematically shown in Fig. 19(a), because the orientation affects the overlap of the wave functions at the interface.<sup>116</sup> Although ellipsometry cannot detect the orientation



Fig. 19 Target issues to be solved in future. Schematics are shown as guides for understanding of the issues discussed in Section 6. (a) Effect on charge injection at interfaces. (b) Advantage of horizontal orientation in OPVs. (c) Index ellipsoid in anisotropic films. (d) Further molecular alignment and ordering as in single crystals.

only at the interface, such as in a monolayer, we can expect analysis by other methods to explain and clarify the effect at interfaces. Since the effects of molecular orientation of polycrystalline materials at interfaces have been investigated,<sup>117,118</sup> we should extend their methods and discussions to the orientation of amorphous materials at interfaces in OLEDs.

#### (3) Application to other organic semiconductor devices

Molecular orientation is commonly one of the critical viewpoints in research on organic devices other than OLEDs, such as organic thin-film photovoltaics (OPVs) or organic field-effect transistors (OFETs). From the electrical viewpoint, the horizontal orientation is preferable in OLEDs and OPVs for charge transport in the direction of thickness, and the vertical orientation is preferable in OFETs for lateral charge transport. From the optical viewpoint, the horizontal orientation is also preferable for both OLEDs and OPVs. As in the case of OLEDs where the light outcoupling is enhanced by the horizontal orientation, the absorption of vertically incident light by OPVs is enhanced by the horizontal orientation of absorbing materials because the transition dipole moments of absorbing molecules are parallel to the electric field of the incident light as shown in Fig. 19(b). The high absorption makes it possible to absorb sufficient light with small thickness, which can compensate for the short exciton diffusion length and the low mobility of OPV materials. Some amorphous OPV materials having a linear or planar shape were recently reported,<sup>119,120</sup> and they can be expected to be oriented horizontally as OLED materials. Although the carrier mobilities in amorphous films are generally lower than those in polycrystalline films which are usually used in OPVs, the horizontal orientation in amorphous films is optically better than vertical orientation of polycrystalline materials.<sup>26-28</sup> In addition, it is highly possible that smooth interfaces of amorphous films without any grain boundary improve fill factors of OPVs.<sup>119,120</sup> The elucidation of the effects in OPVs is a promising theme in research on organic devices.

### (4) Effect of optical anisotropy on the optical properties of devices

In this article, two kinds of effects on device performance were discussed. One is the effect of the orientation of charge transport materials on the electrical properties of films, and the other is the effect of the orientation of emitting materials on the optical properties of OLEDs. However, the effect of the orientation of charge transport materials on the optical properties of OLEDs has not been discussed sufficiently. To consider this effect, it should be noted that large optical anisotropy of the charge transport layer affects the light propagation in the layer.<sup>31</sup> The refractive index for light polarized parallel to a substrate surface [transverse electric (TE)-polarized light] is equal to  $n_0$ , but that for light with the polarization plane perpendicular to a substrate surface [transverse magnetic (TM)-polarized light] depends on the direction of the wave vector. As shown in Fig. 19(c), this is represented by the equation of the index ellipsoid,<sup>121</sup>

1

$$n_{\rm TE} = n_{\rm o} \tag{2}$$

$$\frac{1}{n_{\rm TM}(\phi)^2} = \frac{\cos^2 \phi}{n_{\rm o}^2} + \frac{\sin^2 \phi}{n_{\rm e}^2}$$
(3)

where  $n_{\text{TE}}$  and  $n_{\text{TM}}$  are the refractive indices for TE- and TMpolarized light, respectively, and  $\phi$  is the angle between the direction normal to the substrate plane and the wave vector of the light. This effect requires modifications to the simulation of light propagation in both OLEDs and OPVs. When the optical anisotropy of a layer in a device is significant, we should include this effect in the optical simulation to estimate precisely the light outcoupling efficiency of OLEDs and the light absorption efficiency of OPVs. It should also be noted that the large optical anisotropy by the horizontal orientation leads to the significantly high refractive index for the TE-polarized light, which is preferable for optimizing the interference effect in OLEDs and OPVs using thin layers, as mentioned previously.<sup>14</sup>

#### (5) Further alignment of molecules by simple fabrication

Although the horizontal molecular orientation affects the device performance positively, the orientation in the plane is random as shown in Fig. 19(d). This means that the molecular orientation in the films is not perfect. It is, of course, preferable to align the molecular axis only in one direction without defects in the film as in single crystals of organic semiconductor materials. Actually, the carrier mobility in single crystals is much higher than that of vacuum-deposited amorphous films.63-65 It was also reported that OLEDs fabricated using single crystals showed high performance,<sup>122</sup> though the size of the device is limited due to the difficulty of fabricating a thin single crystal with a large area. What is important for wide application in the future is to fabricate such a high-performance OLED with a large area by a simple process. The understanding and use of the intermolecular interaction seems essential for it. By deriving the maximum potential of molecular interaction of organic semiconductor materials, this challenge will be successfully overcome in future.

By solving the above issues, the performance of organic devices will be further improved, and the fundamentals of

organic devices will be much more sophisticated from the viewpoint of both chemistry and physics, as with silicon devices. We believe that such fundamental studies in organic semiconductor devices are critical for making them widely available in our daily lives in the near future.

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